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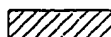
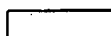
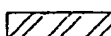
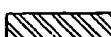
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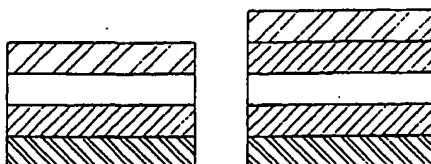
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(54) Title: A MULTI-LAYERED POLYMER ELECTROLYTE AND LITHIUM SECONDARY BATTERY COMPRISING THE SAME

-  GELLED POLYMER ELECTROLYTE
-  POLYMER ELECTROLYTE, PP, PE, PVDF or NON-WOVEN FABRIC
-  CATHODE (+)
-  ANODE (-)



(57) Abstract: The present invention relates to a multi-layered polymer electrolyte and lithium secondary battery comprising the same, wherein the multi-layered polymer electrolyte comprises: A) a separator layer formed of polymer electrolyte, PP, PE, PVdF or non-woven fabric, wherein the separator layer having two surfaces; B) at least one gelled polymer electrolyte layer located on at least one surface of the separator layer comprising: a) 5-90 wt% of PAN-based polymer; b) 5-80 wt% of at least one polymer selected from PVdF-based polymer and PMMA-based polymer; 5-80 wt% of at least one polymer selected from the group consisting of PVC-based polymer and PVdF-based polymer; and C) organic electrolyte solution in which lithium salt is dissolved in a solvent.



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**A MULTI-LAYERED POLYMER ELECTROLYTE AND
LITHIUM SECONDARY BATTERY COMPRISING THE SAME**

TECHNICAL FIELD

5 The present invention relates to a multi-layered polymer electrolyte and a lithium secondary battery comprising the same. More specifically, the multi-layered polymer electrolyte of the present invention comprises:

A) a separator film layer formed of a polymer electrolyte, PP, PE, PVdF or a non-woven fabric;

10 B) a gelled polymer electrolyte layer which is cast onto one or both surfaces of the separator film layer, comprising:

a) 5 - 90 wt % of PAN group polymer;

b) 5 - 80 wt % of polymer selected from PVdF group polymers and PMMA group polymers;

15 c) 5 - 80 wt % of polymer selected from the group consisting of PVC group polymers and PVdF group polymers; and

C) an organic electrolyte solution in which a lithium salt is dissolved in an organic solvent.

20

BACKGROUND ART

Recently, concomitant with miniaturization and lightweight trends in electronic appliances, research into energy sources having high density and high energy has been performed intensively. A lithium secondary battery has been proposed as one energy source in the aspect that the higher integration

of energy is possible because the molecular weight of lithium used in a lithium secondary battery is very low, but its density is relatively high.

In the earlier developed lithium secondary battery, an anode was fabricated with metallic lithium or lithium alloy. However, a cycle characteristic
5 of such secondary battery using metallic lithium or lithium alloy is reduced significantly due to dendrites generated on an anode in the course of repeated charging and discharging of the battery.

A lithium ion battery was presented in order to solve the problem of dendrite generation. The lithium ion battery developed by SONY Company
10 in Japan and widely used all over the world comprises an anode active material, a cathode active material, an organic electrolyte solution and a separator film.

The separator film functions to prevent an internal short-circuiting of the lithium ion battery caused by contacting of a cathode and an anode, and
15 to permeate ions. Separator films generally used at the present time are polyethylene (hereinafter referred to as "PE") or polypropylene (hereinafter referred to as "PP") separator films. However, the lithium ion battery using the PE or PP separator film has problems such as instability of a battery, intricacy of its fabrication process, restriction on battery shape and limitation of high
20 capacity. There have been attempts to solve the above-mentioned problems, but there is no clear result until now.

On the contrary, a lithium polymer battery uses a polymer electrolyte having two functions, as a separator film and as an electrolyte at the same time, and it is now being viewed with keen interest as a battery being able to

solve all of the problems. The lithium polymer battery has an advantage in view of productivity because the electrodes and a polymer electrolyte can be stacked in a flat-plate shape and its fabrication process is similar to a fabrication process of a polymer film.

5 A conventional polymer electrolyte is mainly prepared with polyethylene oxide (hereinafter referred to as "PEO"), but its ionic conductivity is merely 10^{-8} S/cm at room temperature, and accordingly it can not be used commonly.

10 Recently, a gel or hybrid type polymer electrolyte having an ionic conductivity above 10^{-3} S/cm at room temperature has been developed.

 K. M. Abraham *et al.* and D. L. Chua *et al.* disclose a polymer electrolyte of a gel type polyacrylonitrile (hereinafter referred to as "PAN") group in U.S. Patent No. 5,219,679 and in U.S. Patent No. 5,240,790 respectively. The gel type PAN group polymer electrolyte is prepared by
15 injecting a solvent compound (hereinafter referred to as an "organic electrolyte solution") prepared with a lithium salt and organic solvents, such as ethylene carbonate and propylene carbonate, etc. into a polymer matrix. It has the advantages that the contact resistance is small in charging/discharging of a battery and desorption of the active materials rarely
20 takes place because the adhesive force of the polymer electrolyte is good, and accordingly adhesion between a composite electrode and a metal substrate is well developed. However, such a polymer electrolyte has a problem in that its mechanical stability, namely its strength, is low because the electrolyte is a little bit soft. Especially, such deficiency in strength may

cause many problems in the fabrication of an electrode and battery.

A. S. Gozdz *et al* discloses a polymer electrolyte of hybrid type polyvinylidenedifluoride (hereinafter referred to as "PVdF") group in U.S. Patent No. 5,460,904. The polymer electrolyte of the hybrid type PVdF group
5 is prepared by fabricating a polymer matrix having a porosity not greater than submicron, and then injecting an organic electrolyte solution into the small pores in the polymer matrix. It has the advantages that its compatibility with the organic electrolyte solution is good, the organic electrolyte solution injected into the small pores is not leaked so as to be safe in use and the
10 polymer matrix can be prepared in the atmosphere because the organic electrolyte solution is injected later. However, it has the disadvantages that the fabrication process is intricate because when the polymer electrolyte is prepared, an extraction process of a plasticizer and an impregnation process of the organic electrolyte solution are required. In addition, it has a critical
15 disadvantage in that a process forming a thin layer by heating and an extraction process are required in fabrication of electrodes and batteries because the mechanical strength of the PVdF group electrolyte is good but its adhesive force is poor.

Recently, a polymer electrolyte of a polymethylmethacrylate
20 (hereinafter referred to as "PMMA") group was presented in *Solid State Ionics*, 66, 97, 105 (1993) by O. Bohnke and G. Frand *et al*. The PMMA polymer electrolyte has the advantages that it has an ionic conductivity of 10^{-3} S/cm at room temperature and its adhesive force and compatibility with an organic electrolyte solution are good. However, it is not suitable for lithium

polymer batteries because its mechanical strength is very poor.

In addition, a polymer electrolyte of a polyvinylchloride (hereinafter referred to as "PVC") group, which has good mechanical strength and has an ionic conductivity of 10^{-3} S/cm at room temperature, was presented in J.

5 *Electrochem. Soc.*, 140, L96 (1993) by M. Alamgir and K. M. Abraham. However, it has problems of a poor low-temperature characteristic and a high contact resistance.

Recently, new methods to complement disadvantages of lithium ion batteries and lithium polymer batteries have been attempted. U.S. Patent No. 10 5,681,357, U.S. Patent No. 5, 688,293 and U.S. Patent No. 5,834,135M to Oliver *et al.* disclose a fabrication method of secondary battery, comprising the steps of placing a separator film obtained by casting a solution, in which a polymer such as PVdF, etc. is dissolved in an organic solvent or an organic electrolyte solution, onto a PP or PE separator film used for a lithium ion 15 battery between an anode and a cathode, making the resultant into one body by a certain heat lamination process and then injecting an organic electrolyte solution into the body. However, such method has disadvantage that deformation of the PP or PE separator film is caused and pores of the separator film are closed because a polymer solution is cast onto the PP or 20 PE separator film. In addition, because electrodes and the separator film are made into one body by a heat lamination process, contact with each other is insufficient, and therefore, a contact resistance is increased. Due to the above disadvantages, high rate charge and discharge characteristics of the batteries are poor and cycle life characteristics of the batteries are lowered. In U.S.

Patent No. 5,691,005 and U.S. Patent No. 5,597,659, Kenichi Morigaki *et al.* disclose a method for inhibiting a cycle life of a batteries by restraining the generation of dendrite of lithium when metallic lithium or a lithium alloy is used as an anode. Such effect is achieved by injecting a ultraviolet (hereinafter referred to as "UV") curable oligomer or monomer into a PE separator film and then irradiating UV rays onto the resultant, to generate a gelled polymer electrolyte at pores in the PE separator film. However, in such method, although it is possible to improve cycle life, a resistance is increased compared with the one in which an organic electrolyte solution is impregnated into the PE separator film because a polymer electrolyte is injected into the pores of the PE separator film. Accordingly, charge and discharge characteristics of the lithium secondary batteries are lowered. In addition, its adhesive force with an electrode is inferior, and therefore, a fabrication of a battery becomes intricate.

15

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide an electrolyte for a lithium secondary battery which is superior in adhesion with electrodes, compatibility with an organic electrolyte solution for a lithium secondary battery, mechanical strength and permeability, etc.

20

Another object of the present invention is to provide a lithium secondary battery comprising said electrolyte.

The above and other objects of the present invention can be achieved by providing a multi-layered polymer electrolyte in which a gelled polymer

electrolyte showing good adhesion with electrodes, good compatibility with an organic electrolyte solution for a lithium secondary battery, high mechanical strength and permeability, etc. is cast onto one or both surfaces of a separator film, for example, a polymer electrolyte, PP, PE, PVdF, non-woven fabric, etc. In more detail, the above and other objects of the present invention can be achieved by providing a multi-layered electrolyte, comprising:

A) a separator film layer formed of a polymer electrolyte, PP, PE, PVdF or a non-woven fabric;

B) a gelled polymer electrolyte layer which is cast onto one or both surfaces of the separator film layer, comprising:

a) 5 - 90 wt % of PAN group polymer;

b) 5 - 80 wt % of polymer selected from the group consisting of PVdF group polymers and PMMA group polymers;

c) 5 - 80 wt % of polymer selected from the group consisting of PVC group polymers and PVdF group polymers; and

C) an organic electrolyte solution in which a lithium salt is dissolved in an organic solvent.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1a and 1b are cross-sectional views illustrating a multi-layered polymer electrolyte according to the present invention.

Figure 2a and 2b are cross-sectional views illustrating a lithium secondary battery comprising the multi-layered polymer electrolyte according to the present invention.

Figures 3a - 3c are process flow diagrams illustrating fabrication of lithium secondary batteries according to the present invention.

Figure 4 is a graph showing charge and discharge characteristics of the lithium secondary batteries of Examples 1 - 6 and Comparative Examples 1 and 2.

Figure 5a is a graph showing high-temperature characteristics of the lithium secondary battery obtained in Example 2, and Figure 5b is a graph showing high-temperature characteristics of the lithium secondary battery obtained in Comparative Example 2.

Figure 6a is a graph showing high-rate discharge characteristics of the lithium secondary battery obtained in Example 2, and Figure 6b is a graph showing high-rate discharge characteristics of the lithium secondary battery obtained in Comparative Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a multi-layered polymer electrolyte and a lithium secondary battery comprising the same. Said multi-layered polymer electrolyte comprises:

A) a separator film layer formed of a polymer electrolyte, PP, PE, PVdF or a non-woven fabric;
B) a gelled polymer electrolyte layer which is cast onto one or both surfaces of the separator film layer, comprising:

- a) 5 - 90 wt % of PAN group polymer;
- b) 5 - 80 wt % of polymer selected from the group consisting of PVdF

group polymers and PMMA group polymers;

c) 5 - 80 wt % of polymer selected from the group consisting of PVC group polymers and PVdF group polymers; and

C) an organic electrolyte solution in which a lithium salt is dissolved in an
5 organic solvent.

The PAN group polymers used in the present invention are superior in adhesion with electrodes and ion conductivity. The PVdF group and the PMMA group polymers are superior in compatibility with an organic electrolyte. The PVC group and the PVdF group polymers are superior in
10 mechanical strength. Accordingly, the present invention provides a polymer electrolyte showing superior characteristics. The polymer electrolyte of the present invention can be prepared by casting a combination of polymers having good adhesion with electrodes, good compatibility with an organic electrolyte solution for a lithium secondary battery and high mechanical
15 strength onto one or both surfaces of a separator film.

It is preferred that the PAN group polymer is selected from the group consisting of polyacrylonitrile and poly(acrylonitrile-methylacrylate), the PMMA group polymer is selected from the group consisting of polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate) and
20 poly(methylmethacrylate-co-methacrylic acid), the PVdF group polymer is selected from the group consisting of polyvinylidene difluoride, poly(vinylidene difluoride-hexafluoropropylene) and the PVC group polymer is selected from the group consisting of polyvinylchloride and poly(vinyl chloride-co-acrylonitrile).

A mixing ratio of a polymer mixture can be varied according to the characteristics required. When good adhesive force with electrodes is required, a ratio of the polymer component a) is increased. When compatibility with an organic electrolyte solution is required, a ratio of the polymer component b) is increased. When good mechanical strength is required, a ratio of the polymer component c) is increased.

Lithium salts used in the present invention are the same as generally used in the lithium secondary batteries, such as LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 and LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$. Among them, LiPF_6 is more preferable.

Examples of an organic solvent used in the organic electrolyte solution may be ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate or mixtures thereof. In order to improve the low-temperature characteristics, an additional solvent, such as methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, butylene carbonate, γ -butyrolactone, 1,2-dimethoxyethane, dimethylacetamide, tetrahydrofuran or mixtures thereof, can be added to the above organic solvent.

The polymer electrolyte according to the present invention can further comprise a plasticizer, a porous filler, etc.

Examples of the plasticizer may include N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), propylene carbonate (PC), acetonitrile and mixtures thereof, but not limited thereto. The amount of the plasticizer used for the polymer electrolyte is preferably adjusted in the range

of 100 - 2000 wt % of the total polymer mixture.

Examples of the filler include TiO_2 , BaTiO_3 , Li_2O , LiF , LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE, an organic filler, a polymer filler and mixtures thereof. The filler improves porosity and mechanical strength of the electrolyte. Generally, the content of the filler is no more than 20 wt % of the total polymer mixture.

A preparation method of the gelled polymer electrolyte layer, comprising:

a) a step of sufficiently mixing (generally, for 12 hours) 5 - 90 wt % of PAN group function-I polymers, 5 - 80 wt % of function-II polymers selected from the group consisting of PVdF group and PMMA group polymers and 5 - 80 wt % of function-III polymers selected from the group consisting of PVC and PVdF group polymers, and optionally with 100 - 2000 wt % of a plasticizer, 100 - 2000 wt % of an organic electrolyte solution and/or no more than 20 wt % of a porous filler (for example, SiO_2 , etc.) to the above polymer mixture, respectively;

b) a step of obtaining a homogeneous solution having a viscosity of 10,000 - 60,000 cps by heating the resulting homogeneous mixture at 80 - 180°C for 10 minutes to 2 hours; and

c) a step of generating a gelled polymer film by casting the obtained homogeneous solution by a die-casting or a doctor blade method.

An important factor in polymer blending is a solubility parameter. According to CRC Handbook of Polymer-Liquid Interaction Parameter and Solubility Parameters written by A.F.M. Baton *et al.*, Hilderbrand Parameters

are 23.3 - 31.5 MPa^{1/2} in PAN, 18.6 - 26.3 MPa^{1/2} in PMMA, 12 - 30 MPa^{1/2} in P(VdF-HPP) which is a PVdF group polymer, 19.1 - 22.1 MPa^{1/2} in PVC. Accordingly, by identifying an suitable plasticizer, solvent and blending condition, a homogeneous gelled polymer electrolyte layer can be prepared.

5 Figure 1a and 1b illustrate cross-sectional structures of a multi-layered polymer electrolyte according to the present invention, in which a gelled polymer electrolyte prepared by the above-described method is cast onto one or both surfaces of a separator film, such as a polymer electrolyte, PP, PE, PVdF and a non-woven fabric, etc. In more detail, Figure 1a shows a cross-
10 sectional structure of a double-layered polymer electrolyte in which a gelled polymer electrolyte according to the present invention is cast onto one surface of a separator film such as a polymer electrolyte having good mechanical strength, PP, PE, PVdF or a non-woven fabric. Figure 1b shows a cross-
15 sectional structure of a triple-layered polymer electrolyte in which a gelled polymer electrolyte according to the present invention is cast onto both surfaces of a separator film such as a polymer electrolyte having good mechanical strength, PP, PE, PVdF or a non-woven fabric.

 Figure 2a shows a lithium secondary battery having a mono-cell structure in which the multi-layered polymer electrolyte is located between an
20 anode and a cathode. Figure 2b shows a cross-section of a lithium secondary battery having a bi-cell structure.

 Fabrication processes of lithium secondary batteries using the multi-layered polymer electrolyte are as shown in Figures 3a - 3c. It will now be described in more detail. A solution of gelled polymer electrolyte is cast onto

one or both surfaces of a separator film such as a polymer electrolyte, PP, PE, PVdF, a non-woven fabric or the like at a thickness of 1 - 50 μm , to fabricate a double or triple-layered polymer electrolyte. The obtained multi-layered polymer electrolyte is adhered to both surfaces of the anode or
5 inserted between an anode and a cathode and then adhered, and the resultant is cut so as to be 3 cm \times 4 cm in size, stacked, and then inserted into a vacuum casing. An electrolyte organic solution used in the conventional lithium ion battery is injected into the vacuum casing to impregnate into pores in the anode and the cathode, and the separator film. The vacuum casing is
10 then vacuum-sealed, to fabricate a lithium secondary battery. Adhesive lamination process and the stacking process as shown in Figure 3 will now be described in detail. In Figure 3(a), a solution of a gelled polymer electrolyte is cast onto one surface of a separator film such as a polymer electrolyte, PP, PE, PVdF, a non-woven fabric or the like to obtain a double-layered polymer
15 electrolyte. The obtained polymer electrolyte is closely adhered to both surfaces of an anode. The doubled-layered polymer electrolyte and anode are made into one body by a lamination process. The resultant is cut so as to be in a predetermined size and then stacked it with a cathode in a predetermined size, to fabricate a lithium secondary battery.

20 In Figure 3(b), a solution of a gelled polymer electrolyte is cast onto both surfaces of a separator film such as a polymer electrolyte, PP, PE, PVdF, a non-woven fabric or the like to obtain a triple-layered polymer electrolyte. The obtained polymer electrolyte is adhered to both surfaces of an anode, and then the triple-layered polymer and anode are made into one

body by a lamination process. The resultant is then cut so as to be in predetermined size and then stacked it with a cathode in a predetermined size, to fabricate a lithium secondary battery.

In Figure 3(c), a solution of a gelled polymer electrolyte is cast onto both surfaces of a separator film such as a polymer electrolyte, PP, PE, PVdF, a non-woven fabric or the like to obtain a triple-layered polymer electrolyte. The obtained polymer electrolyte is adhered to both surfaces of an anode, and then a cathode is adhered onto the outside parts of the polymer electrolyte. The resultant is then made into one body in a by-cell structure which consists of a cathode/a triple-layered polymer electrolyte/an anode/a triple-layered polymer electrolyte/a cathode by a lamination process. The resulting plate is cut and then stacked, to fabricate a lithium secondary battery.

Herein, the anode and cathode used in lithium secondary batteries are fabricated as in the conventional art by mixing a certain amount of active materials, conducting materials, binders and an organic solvent, casting the resulting mixture onto both sides of a copper or aluminum foil plate grid, and then drying and rolling. In more detail, an anode consists of one material selected from the group consisting of graphite, cokes, hard carbon, tin oxide and lithiated compounds thereof, metallic lithium or lithium alloys. A cathode consists of one material selected from the group consisting of LiClO_2 , LiNiO_2 , LiNiCoO_2 , LiMn_2O_4 , V_2O_5 and V_6O_{13} .

An organic electrolyte solution used in the fabrication of the battery is a solution selected from the group consisting of a lithium salt-dissolved

ethylene carbonate-dimethyl carbonate (EC-DMC) solution, lithium salt-dissolved ethylene carbonate-diethyl carbonate (EC-DEC) solution, lithium salt-dissolved ethylene carbonate-ethyl methyl carbonate (EC-EMC) solution, lithium salt-dissolved ethylene carbonate-propylene carbonate (EC-PC) solution and mixtures thereof, and solutions in which at least one solvent selected from the group consisting of methyl acetate (MA), methyl propionate (MP), ethyl acetate (EA), ethyl propionate (EP), butylene carbonate (BC), γ -butyrolactone (γ -BL), 1,2-dimethoxyethane (DME), dimethylacetamide (DMA) and THF (tetrahydrofuran) is respectively added to the above lithium salt-dissolved solution.

As a copper and aluminum grid, a plate, a punched plate, an expanded plate and a porous plate can be used. If an organic electrolyte solution is injected after stacking, it is preferable to use a punched plate, an expanded plate and a porous plate for efficient electrolyte impregnation.

EXAMPLES

The present invention will be better understood from the below examples, but those examples are given only to illustrate the present invention, not to limit the scope of it.

Example 1

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000) and 2g of polyvinylidenedifluoride (Atochem Kynar 761), 25g of 1M LiPF_6 solution in EC-DMC was added. The resulting

mixture was mixed for 12 hours. The resulting mixture was then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 which was suitable for casting. The obtained polymeric solution was cast onto one surface of a PE separator film by a die-casting method to prepare a double-layered polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto a graphite anode and then joined with the graphite anode by a lamination process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it was alternately stacked with a LiCoO₂ cathode of 2.9 cm × 3.9 cm in size. Terminals were welded onto the electrodes and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 2

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000) and 2g of polyvinylidenedifluoride (Atochem Kynar 761), 25g of 1M LiPF₆ solution in EC-DMC was added. The resulting mixture was mixed for 12 hours and then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 cps which was suitable for casting. The obtained polymeric solution was cast onto both surfaces of a PE separator film by a die-casting method to prepare a triple-layered polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode. A LiCoO₂ cathode was then adhered onto both surfaces of the obtained plate. The

resultant was cut so as to be 3 cm × 4 cm in size, and then stacked in a bi-cell structure. Terminals were welded onto the electrodes, and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to
5 fabricate a lithium secondary battery.

Example 3

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000) and 2g of polyvinylidenedifluoride (Atochem Kynar 761), 25g of 1M LiPF₆ solution in EC-DMC was added. The resulting
10 mixture was mixed for 12 hours and then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 which was suitable for casting. The obtained polymeric solution was cast onto both surfaces of a PE separator film by a die-casting method to prepare a triple-layered
15 polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode, a LiCoO₂ cathode was adhered onto the both surfaces of the obtained plate, and then the resultant were joined together by a lamination process. The obtained was cut so as to be 3 cm × 4 cm in size and then stacked it in a bi-cell structure.
20 Terminals were welded onto the electrodes and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

25 Example 4

To a mixture of 1g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000), 2g of polyvinylidenedifluoride (Atochem Kynar 761) and 1g of polymethylmethacrylate (available from Polyscience Co., molecular weight of 100,000), 25g of 1M LiPF_6 solution in EC-DMC was added. The resulting mixture was mixed for 12 hours and then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 which was suitable for casting. The obtained polymeric solution was cast onto both surfaces of a PE separator film by a die-casting method to prepare a triple-layered polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode and then joined with the graphite anode by a lamination process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it was alternately stacked with a LiCoO_2 cathode of 2.9 cm × 3.9 cm in size. Terminals were welded onto the electrodes, and then the cell was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 5

To a mixture of 1g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000), 2g of polyvinylidenedifluoride (Atochem Kynar 761) and 0.1g of TiO_2 , 25g of 1M LiPF_6 solution in EC-DMC was added. The resulting mixture was mixed for 12 hours and then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 which was suitable for casting. The obtained polymeric solution was cast onto both

surfaces of a PP separator film by a die-casting method to prepare a triple-layered polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode and then joined with the graphite anode by a lamination process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it was alternately stacked with a LiCoO₂ cathode of 2.9 cm × 3.9 cm in size. Terminals were welded onto the electrodes and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

10

Example 6

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co., molecular weight of 150,000), 2g of polyvinylidenedifluoride (Atochem Kynar 761) and 0.1g of TiO₂, 25g of 1M LiPF₆ solution in EC-DMC was added. The resulting mixture was mixed for 12 hours and then heated at 130°C for one hour to give a clear polymeric solution having a viscosity of about 3000 which was suitable for casting. The obtained polymeric solution was cast onto one surface of a PVdF separator film by a die-casting method to prepare a double-layered polymer electrolyte. The prepared double-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode and then joined with the graphite anode by a lamination process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it was alternately stacked with a LiCoO₂ cathode of 2.9 cm × 3.9 cm in size. Terminals were welded onto the electrodes and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the

25

vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 7

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co.,
5 molecular weight of 150,000) and 2g of polyvinylidenedifluoride (Atochem
Kynar 761), 25g of 1M LiPF_6 solution in EC-DMC was added. The resulting
mixture was mixed for 12 hours and then heated at 130°C for one hour to give
a clear polymeric solution having a viscosity of about 3000 which was suitable
for casting. The obtained polymeric solution was cast onto one surface of a
10 PVdF group gelled polymer electrolyte (prepared by casting after PVdF was
dissolved in an organic solvent electrolyte as in the conventional art) by a die-
casting method to prepare a double-layered polymer electrolyte. The prepared
double-layered polymer electrolyte was closely adhered onto both surfaces
of a graphite anode and then joined with the graphite anode by a lamination
15 process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it
was alternately stacked with a LiCoO_2 cathode of 2.9 cm × 3.9 cm in size.
Terminals were welded onto the electrodes and then the cell was inserted into
a vacuum casing. A 1M LiPF_6 solution in EC-EMC was injected into the
vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate
20 a lithium secondary battery.

Example 8

To a mixture of 2g of polyacrylonitrile (available from Polyscience Co.,
molecular weight of 150,000) and 2g of polyvinylidenedifluoride (Atochem
25 Kynar 761), 25g of 1M LiPF_6 solution in EC-DMC was added, and the

resulting mixture was mixed for 12 hours. When a viscosity of several thousands cps suitable for casting was obtained, the obtained polymeric solution was cast onto both surfaces of a PTFE woven fabric by a die-casting method to prepare a triple-layered polymer electrolyte. The prepared triple-layered polymer electrolyte was closely adhered onto both surfaces of a graphite anode and then joined with the graphite anode by a lamination process. The resultant was cut so as to be 3 cm × 4 cm in size, and then it was alternately stacked with a LiCoO₂ cathode of 2.9 cm × 3.9 cm in size. Terminals were welded onto the electrodes and then the cell was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-EMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

Comparative Example 1

Electrodes and separator films were stacked in order of anode, PE separator film, cathode, PE separator film and anode, terminals were welded onto the electrodes. The obtained cell was inserted into a vacuum casing, a 1M LiPF₆ solution in EC-EMC was injecting a into the casing, and then the casing was vacuum-sealed, to fabricate a lithium secondary battery.

Comparative example 2

According to the conventional preparation method of a gel-polymer electrolyte, 9g of 1M LiPF₆ solution in EC-PC was added to 3g of polyacrolinitrile. The resulting mixture was mixed for 12 hours and then heated at 130°C for 1 hour to obtain a polymer electrolyte matrix. When a

viscosity of 30,000 cps suitable for casting was obtained, the resulting solution was cast by die-casting to give a polymer electrolyte film. A graphite anode, the polymer electrolyte film, a LiCoO_2 cathode, the polymer electrolyte film and a graphite anode were stacked in order. Terminals were welded onto the electrodes, and then the obtained cell was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-EMC was injected into the casing, and then the casing was vacuum-sealed, to fabricate a lithium secondary battery.

Example 9

Test Results

Electrode capacities and cycle life based on the cathode of the lithium secondary batteries obtained in Examples 1 - 8 and Comparative Examples 1 and 2 were examined. These tests were performed with a charge/discharge method of charging the batteries with a C/2 constant current and 4.2V constant voltage, and then discharging with a C/2 constant current. Figure 4 shows the results. As shown in Figure 4, the electrode capacities and cycle life of the lithium secondary batteries of Examples 1 - 8 were superior to the lithium secondary batteries of Comparative Examples 1 and 2. In addition, the lithium secondary batteries of Examples 1 - 8 of the present invention exhibited superior characteristics in that their electrode capacities were not reduced regardless of repeated charge and discharge. Accordingly, it was discovered that the multi-layered polymer electrolyte of the present invention can improve the electrode capacities and cycle life of the lithium secondary batteries. Such improvement seems to be resulted from which surface resistance was reduced because adhesive force between the electrodes and

the multi-layered polymer electrolyte were good, and an ionic conductivity of the polymer electrolyte was also good.

Example 10

5 High rate discharge characteristics of the lithium secondary batteries obtained in Example 2 and Comparative Example 2 were examined. The examination was performed with a charge/discharge method of charging the lithium batteries with a C/2 constant current and 4.2 V constant voltage, and then discharging them while changing the constant current into C/5, C/2, 1C
10 and 2C. Figures 5a and 5b illustrate the results. As shown in Figures 5a and 5b, the lithium secondary battery of Example 1 exhibited capacities of 95% and 90% at 1C and 2C discharge, respectively, based on the value of 0.2C discharge (see Figure 5a). However, the lithium secondary battery of Comparative Example 2 exhibited low capacities of 87% and 56% at 1C and
15 2C discharge, respectively. Accordingly, it was discovered that the high rate discharge characteristic of the lithium secondary battery of Example 2 was superior to that of the lithium secondary battery of Comparative Example 2.

INDUSTRIAL APPLICABILITY

20 The multi-layered polymer electrolyte according to the present invention is superior in adhesive force and mechanical strength to those of the conventional polymer electrolyte. In addition, according to the present invention, a lithium secondary battery showing good performances in low- and high-temperature characteristics, high rate discharge characteristic, capacity

of battery, cycle life, stability, etc. can be provided. Accordingly, the lithium secondary battery can be applied in various industrial fields such as small electronic appliances, communicating apparatus and electric automobiles, etc.

CLAIMS

1. A multi-layered polymer electrolyte for a lithium secondary battery, comprising:

A) a separator film layer formed of a polymer electrolyte, PP, PE, PVdF

5 or a non-woven fabric;

B) a gelled polymer electrolyte layer which is cast onto one or both surfaces of the separator film layer, comprising:

a) 5 - 90 wt % of PAN group polymer;

10 b) 5 - 80 wt % of polymer selected from the group consisting of PVdF group polymers and PMMA group polymers;

c) 5 - 80 wt % of polymer selected from the group consisting of PVC group polymers and PVdF group polymers; and

C) an organic electrolyte solution in which a lithium salt is dissolved in an organic solvent.

15

2. The electrolyte according to claim 1, wherein the PAN group polymer is selected from the group consisting of polyacrylonitrile and poly(acrylonitrile-methylacrylate), the PMMA group polymer is selected from the group consisting of polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate) and poly(methylmethacrylate-co-methacrylic acid), the PVdF group polymer is selected from the group consisting of polyvinylidene difluoride, poly(vinylidene difluoride-hexafluoropropylene) and the PVC group polymer is selected from the group consisting of polyvinylchloride and poly(vinyl chloride-co-acrylonitrile).

3. The electrolyte according to claim 1, wherein the lithium salt is selected from the group consisting of LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and combinations thereof.
- 5.
4. The electrolyte according to claim 1, wherein the organic solvent is ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate or mixtures thereof.
- 10 5. The electrolyte according to claim 4, wherein the organic solvent further comprises a solvent selected from the group consisting of methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, butylene carbonate, γ -butyrolactone, 1,2-dimethoxyethane, dimethylacetamide, tetrahydrofuran and mixtures thereof, in order to improve low-temperature
- 15 characteristic.
6. The electrolyte according to claim 1, wherein the gelled polymer electrolyte layer further comprises a plasticizer or porous filler.
- 20 7. The electrolyte according to claim 6, wherein the plasticizer is selected from the group consisting of N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl carbonate, ethylene carbonate, ethyl methyl carbonate, propylene carbonate, acetonitrile and mixtures thereof.

8. The electrolyte according to claim 6, wherein the porous filler is selected from the group consisting of TiO_2 , BaTiO_3 , Li_2O , LiF , LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE, an organic filler, a polymer filler and mixtures thereof.

5

9. A lithium secondary battery, comprising a cathode, an anode and the electrolyte according to claim 1.

10. The battery according to claim 9, wherein the cathode comprises at least one cathode active material selected from the group consisting of LiCoO_2 , LiNiO_2 , LiNiCoO_2 , LiMn_2O_4 , V_2O_5 and V_6O_{13} .

11. The battery according to claim 9, wherein the anode comprises at least one anode active material selected from the group consisting of graphite, cokes, hard carbon, tin oxide, lithiated compounds thereof, metallic lithium and lithium alloys.

12. The battery according to claim 9, which is in a mono-cell structure.

13. The battery according to claim 9, which is in a bi-cell structure.

FIG. 1

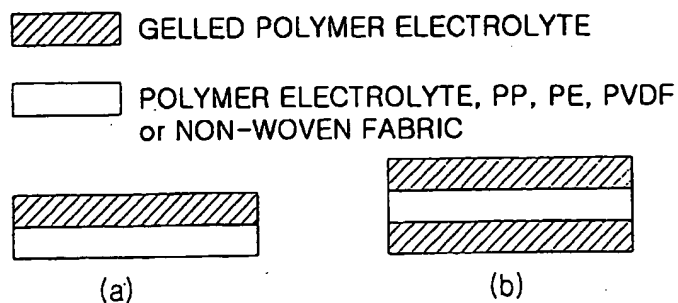


FIG. 2

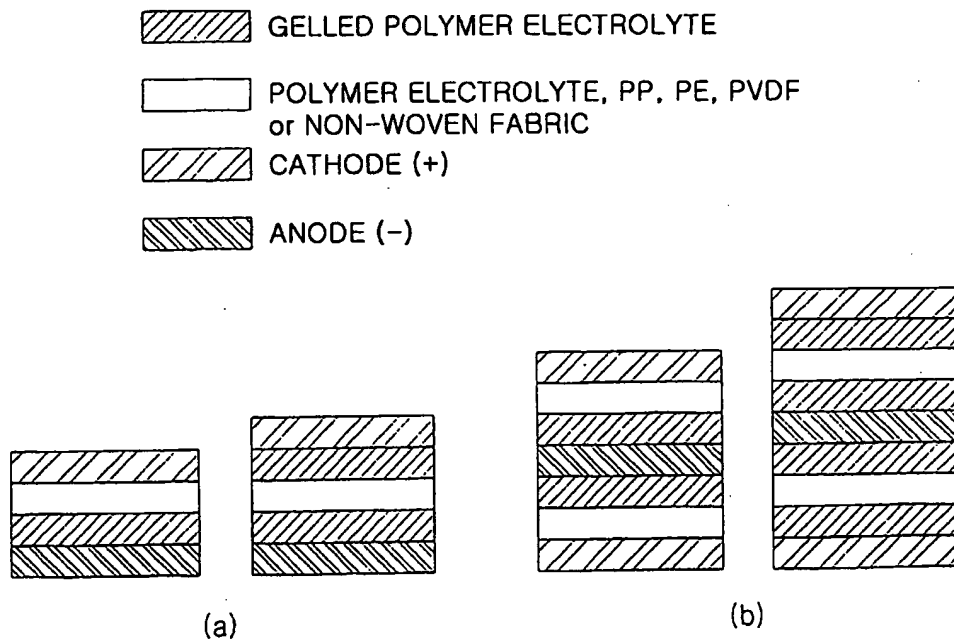


FIG. 3A

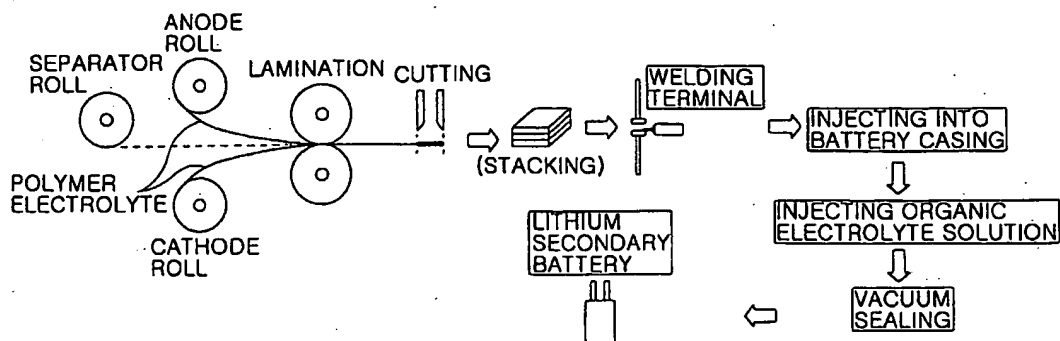


FIG. 3B

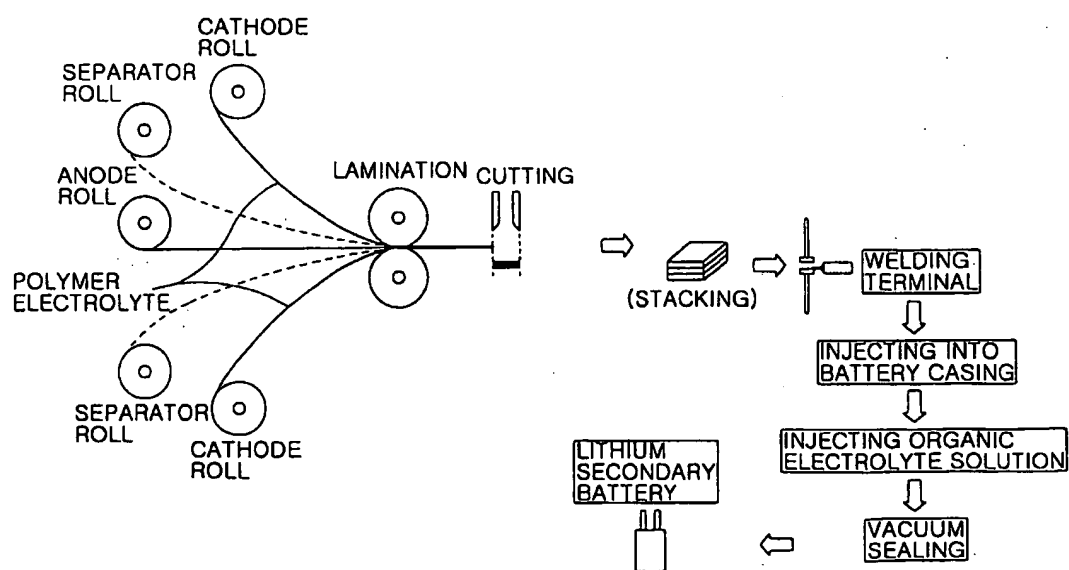


FIG. 3C

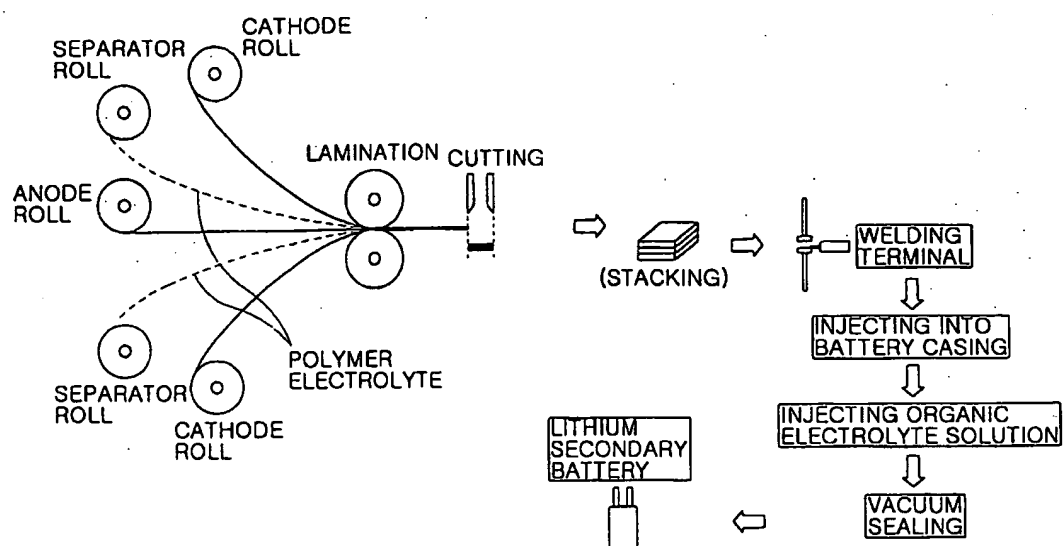


FIG. 4

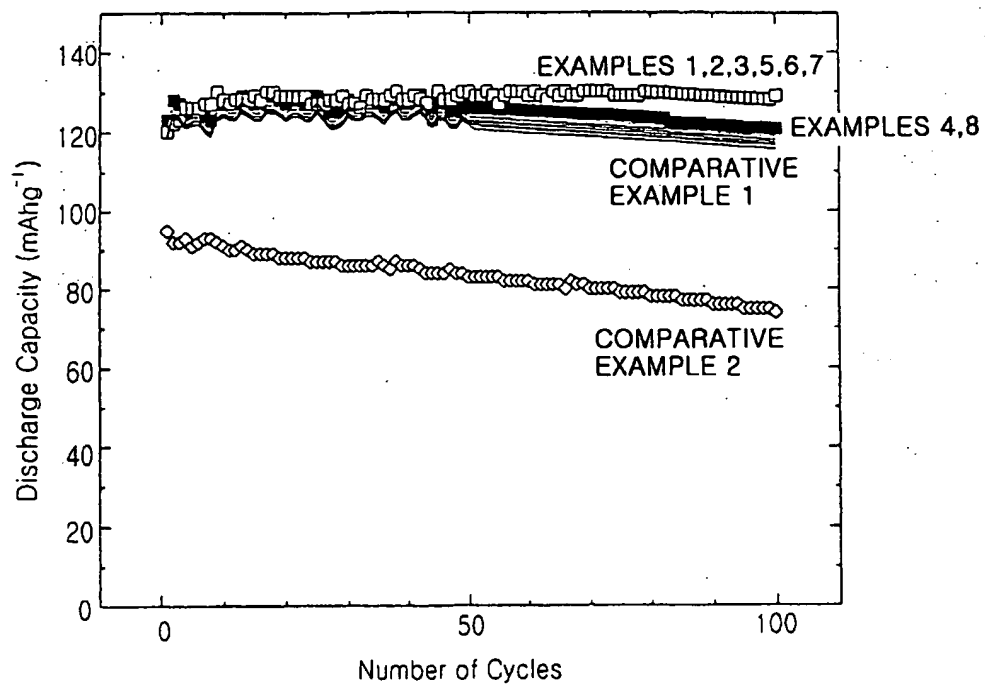


FIG. 5A

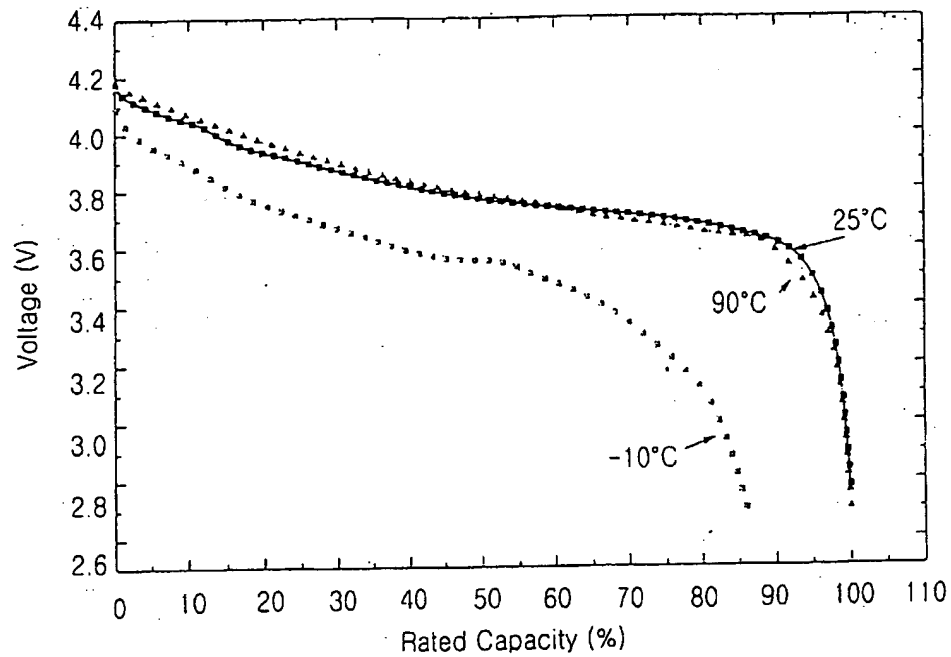


FIG. 5B

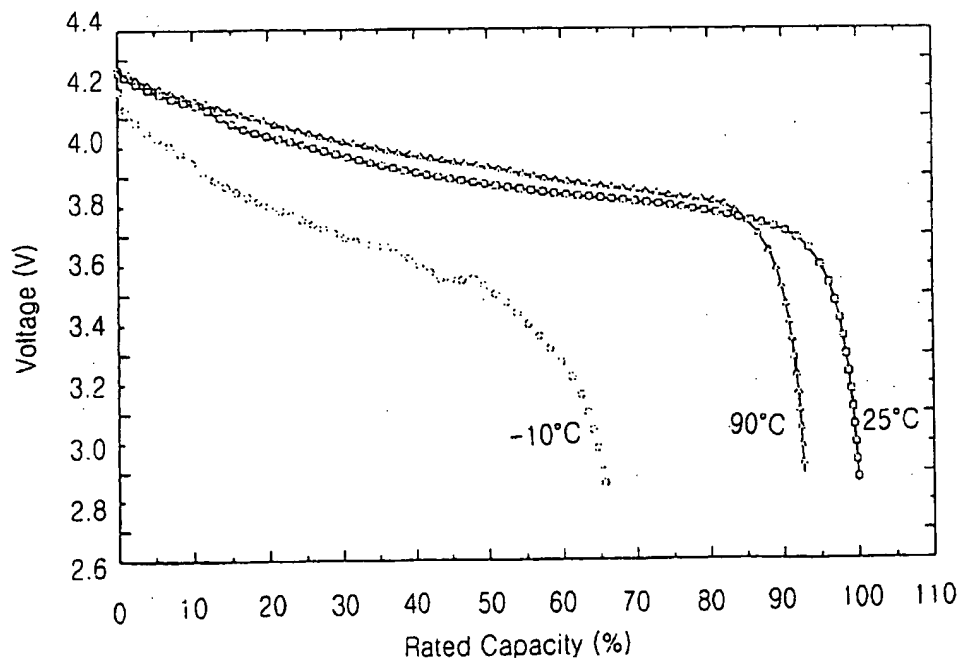


FIG. 6A

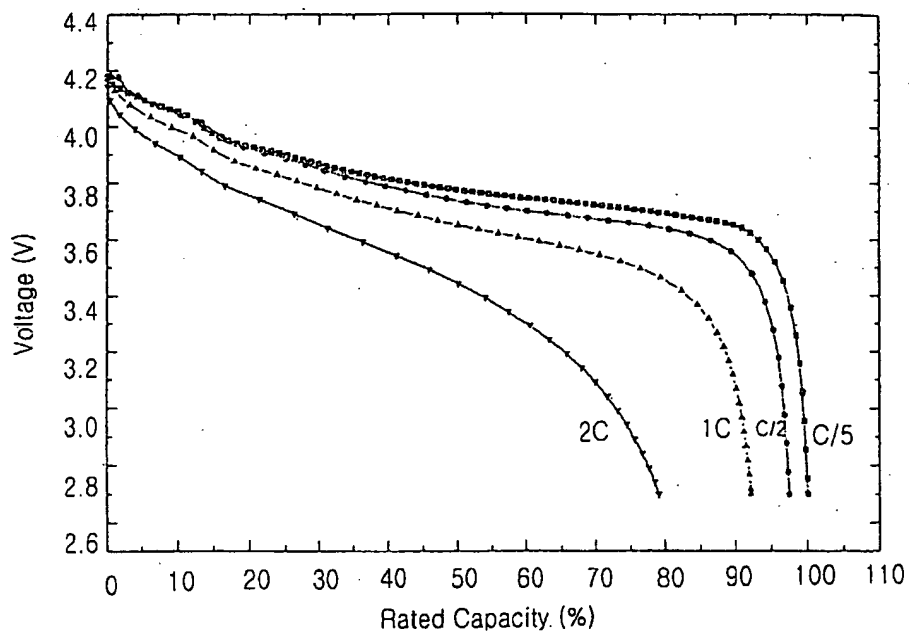
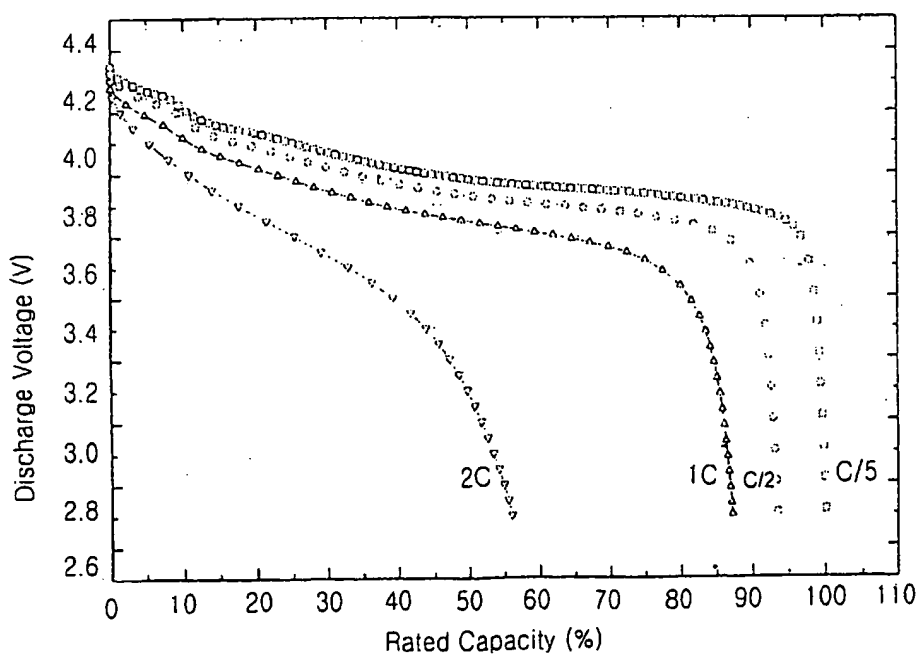


FIG. 6B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/00129**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7 H01M 10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 : H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

KOREAN PUBLICIZED PATENTS

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPAT, FPD, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | KR, A, 1020000003091 (KIST) JAN. 15, 2000 SEE THE WHOLE DOCUMENT | 1-13 |
| X | KR, A, 1020000003092 (KIST) JAN. 15, 2000 SEE THE WHOLE DOCUMENT | 1-13 |
| Y | JP, A, 02144860 (MATSUSHITA ELECTRIC IND CO LTD.) JUNE. 04, 1990 SEE THE WHOLE DOCUMENT | 3 |
| Y | US, A, 06040092 (SHARP KABUSHIKI KAISHA) MAR. 21, 2000 SEE THE WHOLE DOCUMENT | 4 |
| Y | JP, A, 06333597 (SANYO ELECTRIC CO LTD.) DEC. 02, 1994 SEE THE WHOLE DOCUMENT | 5 |
| Y | US, A, 05783333 (POLYSTOR CORPORATION) JULY. 21, 1998 SEE THE WHOLE DOCUMENT | 10 |

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"&" document member of the same patent family

Date of the actual completion of the international search

15 JANUARY 2002 (15.01.2002)

Date of mailing of the international search report

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